Desalination and Water Treatment
www.deswater.com

47 (2012) 112–119
September

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doi: 10.1080/19443994.2012.696807

Major mechanism(s) of chloramine decay in rechloraminated laboratory scale system waters

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Received 3 October 2011; Accepted 26 March 2012

ABSTRACT

Traditionally it is believed that nitrification was solely responsible for the widely observed chloramine loss under nitrifying conditions. On the contrary, recent results have shown that an unidentified agent (soluble microbial products or modified natural organic matter) chemically accelerates chloramine decay in rechloraminated nitrifying samples which were filtered to eliminate microbes. However, how those agents accelerate chloramine decay is not known. Mildly and severely nitrified samples were collected from a laboratory scale system and microbes were separated through filtration and then rechloraminated. To understand the mechanism, simple stoichiometry was employed. In all samples, rechloramination induced ammonia loss possibly by auto-decomposition, especially in the initial stages. In severely nitrified samples, accelerated auto-decomposition and nitrite oxidation were found to be the major mechanisms chemically accelerating the chloramine loss indicating that the agent did not demand appreciable chloramine. However, in the mildly nitrified water, a large discrepancy in chloramine demand what is explainable by stoichiomatye was seen. The natural organic matter (NOM) oxidation was suspected to be the dominant mechanism during the prolonged incubation of mildly nitrified samples. The identification of the agent is important as it highly accelerates chloramine decay.

Keywords: Auto-decomposition; Chloramine; Nitrification; Nitrogenous species; Nitrite oxidation

1. Introduction

To maintain an adequate water quality and protect the public health, disinfectants, mainly chlorine and chloramine, have been used since the early twentieth century. Because of the increased concern over the formation of chlorinated disinfection by-products, many water utilities were forced to use chloramine instead of chlorine. Chloramine is also found to be effective at controlling microbial growth in biofilms and is chemically stable compared to free chlorine [1,2]. Hence, chloramine has been gaining popularity as a disinfectant for drinking water.

Regardless of the advantages of chloramine, a sudden drop in chloramine residual is frequently noticed following an episode of nitrification in a chloraminated

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system. Nitrification is a two step biological conversion of free ammonia to nitrite and then to nitrate in the presence of ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria, respectively. Based on the nitrite level produced by AOB and the chloramine decay rate, Sathasivan [3] defined mildly and severely nitrifying stages in bulk water samples. The stage when chloramine decay was reasonably stable and the nitrite production rate was slow and the level was <0.010 mg-N/L was referred to as the mildly nitrifying stage. The stage when nitrite reached a high level (more than 0.10 mg-N/L) and chloramine decay excessively accelerated (total decay was about one order higher than in the mildly nitrifying stage) was defined as the severely nitrified stage. Hence, the onset of severe nitrification is undesirable.

Nitrification chemically and microbiologically accelerates the chloramine decay [4]. However, the microbial chloramine decay mechanism is yet to be clearly defined. It has been hypothesized that rapid chloramine decay is due to the effect of chloramine reaction with nitrite produced by AOB; alternatively, ammonia oxidation could shift the equilibrium of monochloramine formation so that free ammonia is metabolized and subsequently, monochloramine is hydrolyzed [5,6]. Therefore, both microbial and chemical degradation processes are consequences of each other.

There are several pathways for chemical degradation of chloramine. The stoichiometry of Eq. (1) is attributed to a direct reaction between monochloramine and nitrite or to a reaction between nitrite and hypochloric acid (Eq. (2)) produced by monochloramine hydrolysis. The reaction rate between monochloramine and nitrite is low, but it significantly increases in the presence of bromide [7]. Similarly, auto-decomposition and natural organic matter (NOM) oxidation drive the chemical decay of chloramine. Auto-decomposition follows a set of complex reactions. The generalized form is presented in Eq. (3) [8]. During the auto-decomposition reaction, ammonia in monochloramine is primarily oxidized to nitrogen gas with the formation of smaller quantities of nitrate (Eq. (4)) and possibly some other unknown products [9]. If the sample does not contain microbes, the nitrogen gas formation can be estimated using Eq. (3) after measuring total ammoniacal nitrogen (TAN: sum of NH_2Cl–N, NH_3–N, and NH_4^+–N) loss. Several studies have demonstrated that NOM could be responsible for monochloramine decay [7,10]. The structure of NOM is complex, however, the chloramine demand and major reaction products are simplified assuming that chemical composition of NOM is similar to typical biomass, $C_5H_7O_2N$ [11], and the final products of NOM oxidation are carbon dioxide, bicarbonate, ammonium, and chloride as shown in Eq. (5). Chemical decay of chloramine is controlled by temperature, pH, chlorine to ammonia ratio, initial chloramine residuals, nitrite levels, dissolved organic matter, etc.

$$NH_2Cl + NO_2^- + H_2O \rightarrow NO_3^- + NH_4^+ + Cl^- \tag{1}$$

$$HOCl + NO_2^- \rightarrow NO_3^- + H^+ + Cl^- \tag{2}$$

$$3NH_2Cl \rightarrow N_2 + NH_3 + 3Cl^- + 3H^+ \tag{3}$$

$$4NH_2Cl + 3H_2O \rightarrow 3NH_3 + NO_3^- + 4Cl^- + 5H^+ \tag{4}$$

$$\begin{aligned} &1/10C_5H_7O_2N + NH_2Cl + 9/10\,H_2O \rightarrow 4/10\,CO_2 \\ &\quad + 1/10HCO_3^- + 11/10NH_4^+ + Cl^- \end{aligned} \tag{5}$$

However, in full-scale systems both chemical and microbial decay takes place. Separation of microbial activities and chemical reactions is essential to understand the decay mechanism. Sathasivan [4] developed a simple tool called microbial decay factor (F_m) method, which separately quantified the role of microbes and chemical reactions on chloramine decay. F_m is the ratio between the microbial decay coefficient (k_m) and chemical decay coefficient (k_c). Following the F_m method, Bal Krishna and Sathasivan [12] reported the occurrence of accelerated chemical decay of chloramine under severe nitrification conditions. They further demonstrated either soluble microbial products (SMPs) released by microbes or modified NOM characteristics (due to the microbial activities) were responsible for rapid acceleration.

The chloramine decay due to chemical losses of ammonia and nitrite is not completely understood. Valentine [13] evaluated the disappearance of monochloramine (2.8–106 mg-Cl_2/L) in the presence of nitrite (70–700 mg-N/L). Leung and Valentine [14] have used the rate constant obtained from the reaction between nitrite and hypochloric acid to evaluate the pathways of nitrite loss. However, they used a relatively high monochloramine concentration (21 mg-Cl_2/L). Hao [15] conducted experiment with excessive ammonia (45–900 mg-N/L), nitrite (7.5–118 mg-N/L), and monochloramine residuals (0.43–9.2 mg-Cl_2/L) to determine the kinetics of monochloramine loss in the presence of nitrite. Later on, several models have been developed in order to explain chloramine decay due to nitrite oxidation, auto-decomposition, and reaction with NOM [7,10,16,17].

While the detailed kinetic study is important to evaluate mechanisms thoroughly, a simple stoichiometric analysis may reveal the gaps in our understanding of chloramine decay mechanisms. Depending on the outcome, further research can be directed in establishing the mechanisms of chloramine loss and hence, effective control measures can be designed and practiced. Thus, application of stoichiometry to explain the chemical decay mechanisms in nitrified bulk waters is the first step and hence, the major focus of this study. Mildly and severely nitrified bulk water samples were collected from the laboratory scale system and filtered through 0.2 μm membrane filter to eliminate the microbes. Chloramine was dosed as needed to obtain a known initial condition and chemical decay mechanisms were determined using stoichiometry at various conditions.

2. Materials and methods

2.1. Laboratory scale system setup and operation

Laboratory scale system (Fig. 1) was set up at the Civil Engineering laboratory in Curtin University, Western Australia. The laboratory scale system contained five reactors and they were connected in series. Each reactor was 25 L in total volume and was made of high density polyethylene. Water collected from Mundaring reservoir, Western Australia, was used as feed water. Every day 20 L of water, containing a chloramine residual of 2.5 mg/L (Cl-to-TAN ratio of 4.5:1), was fed continuously to gain a water retention time about 20 ± 2 h in each reactor. Cl is the total chlorine. Water temperature was maintained at 20.0 ± 2.0°C in the first three reactors (R-1 to R-3) and 23.0 ± 2.0°C in the last two reactors (R-4 and R-5) to create various nitrifying conditions, using heating plates installed at the bottom of each reactor. After stable and varying nitrifying conditions (mild and severe), which generally occur in full-scale chloraminated system, were achieved, samples were collected from the reactors and experiments were conducted. The details of the laboratory scale system setup and operation are given in Bal Krishna and Sathasivan [12].

2.2. Experimental design

Sample bottles (600 mL PET, polyethylene terephthalate) and glassware were cleaned by dipping them into a 10% sodium hypochlorite solution for 24 h and followed by rinsing with reverse osmosis treated water until bottles and glassware were free of chlorine. Sample collection glassware, the filtration unit, and the filter papers were autoclaved.

2.2.1. Chemical decay profiles of chloramine in mildly and severely nitrified bulk waters

Bulk water samples representing mildly and severely nitrifying conditions were collected from R-2 and R-5 of a laboratory scale system (Fig. 1), respectively. The samples were filtered through a 0.2 μm polycarbonate membrane filter (cat No. K02CP04700, GE Water and Process Technology) to remove microbes. These samples were put in 600 mL PET bottles. Samples were spiked with total chlorine stock

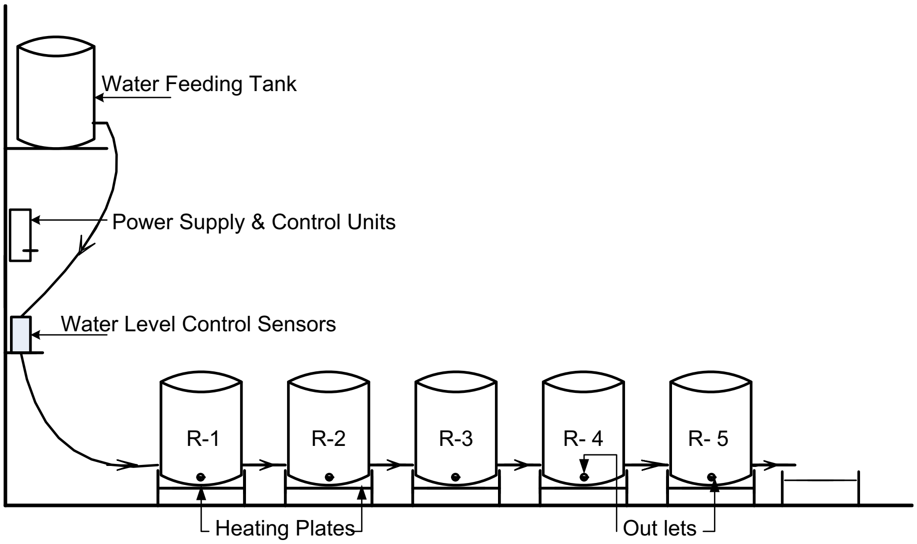

Fig. 1. Laboratory scale system setup (adapted from Bal Krishna and Sathasivan [12]).

solution (500 mg-Cl_2/L) and ammonia stock solution (500 mg-N/L) to achieve a final chloramine residual of 2.0 mg/L (Cl-to-TAN ratio of 4.5:1) and pH was adjusted to 8.0 ± 0.1. All samples were then incubated at a constant temperature (20˚C) in a water bath covered by a lid. Samples were prepared in duplicate. Chemical parameters (total chlorine, TAN, nitrite, nitrate, and pH) were continuously monitored and averages of them were reported.

2.2.2. *Chemical decay profiles of chloramine in mildly nitrified bulk waters after addition of nitrite*

Similar to the above section, bulk water samples were collected from R-2 and they were filtered through 0.2 μm polycarbonate membrane filter (cat No. K02CP04700, GE Water and Process Technology). The samples were then spiked with total chlorine stock solution (500 mg-Cl_2/L) and ammonia stock solution (500 mg-N/L) to achieve a final chloramine residual of 2.0 mg/L (Cl-to-TAN ratio of 4.5:1). Similarly, nitrite stock solution (500 mg-N/L) was spiked to achieve a final nitrite concentration of 0.28 mg-N/L and pH was adjusted to 8.0 ± 0.1. Afterward, samples were incubated in a water bath (20˚C) closed by a lid and chemical parameters were monitored as detailed above.

2.3. *Calculation for determining chloramine decay mechanisms*

Chloramine losses due to nitrite oxidation and auto-decomposition were determined using Eqs. (1) and (3), respectively. According to Eq. (1), when chloramine is lost by nitrite oxidation, 1 mmol of nitrite (14.0 mg-N/L) will result in 1 mmol loss of chloramine (71.0 mg-Cl_2/L). Using this conversion, the chloramine loss due to nitrite oxidation was calculated.

TAN loss from auto-decomposition and Eq. (3) was used to determine the nitrogen gas production. According to Eq. (3), auto-decomposition of 3 mmol of chloramine (3 × 71.0 mg-Cl_2/L) will result in 28.0 mg-N/L of nitrogen loss (converted to nitrogen gas). Using this conversion, chloramine demand exerted by auto-decomposition was calculated.

2.4. *Analytical procedures*

Total chlorine, TAN, nitrite, nitrite + nitrate (NO_x), and dissolved organic carbon (DOC) were measured immediately after collecting samples from the reactor and from sample bottles. The Aquakem 200, a high precision wet chemistry automated analyzer, was employed to measure TAN, nitrite and NO_x concentrations. TAN and NO_x were measured spectrophotometrically according to the methods described in Environmental Protection Authority [18]. Nitrite was measured by the sulfanilamide method (4500-NO_2^- B) APHA [19]. Before measuring NO_x, total chlorine residual was reduced stoichiometrically using 0.5% sodium thiosulphate (analytical grade) stock solution. The analyser had a detection limit for TAN, nitrite, and NO_x of 0.002 mg-N/L. The measurement error for TAN and nitrite was found to be ±1.5% (95% confidence level). NO_x measurement includes the additional experimental error during reduction of chlorine using sodium thiosulphate. Therefore, NO_x measurement error was found to be ±2.0% (95% confidence interval). Total chlorine residuals were measured by the DPD colorimetric method using a HACH pocket colorimeter. The DOC was measured using a Sievers 5310C Laboratory TOC analyzer. A portable pH meter (HACH 40d) was used to measure pH. Details of measurement methods are given in Bal Krishna and Sathasivan [12].

3. Results and discussion

3.1. *Characteristics of bulk water samples collected from the reactors*

Significant drop in chloramine residuals and associated changes in nitrogenous compounds (TAN, nitrite, and nitrate) between R-2 and R-5 were observed because of both chemical reactions and microbial activities (Table 1). Total chlorine maintained in the feed tank was 2.5 ± 0.03 mg/L. When water traveled from the feed tank to R-2, about 0.61 ± 0.06 mg/L of chloramine was lost, i.e. the chloramine residual in R-2 was 1.89 ± 0.03 mg/L. It progressively decayed along the reactors and dropped to 0.11 ± 0.03 mg/L in R-5. Simultaneously, increased nitrite and nitrate levels between R-2 and R-5 demonstrated the establishment of nitrifying bacterial activities that likely had caused the decomposition of chloramine residuals. The NO_x increase between R-2 and R-5 was 0.41 ± 0.006 mg-N/L (Table 1). The difference in NO_x levels clearly indicated that the AOB activity increased with retention time. However, total inorganic nitrogen (TIN: summation of TAN and NO_x) barely changed from R-2 to R-5 indicating that all lost TAN have been converted to NO_x. In addition, a consistent decrease in pH from 7.96 ± 0.1 to 7.64 ± 0.1 was noted between R-2 and R-5, which further confirmed the increase of nitrifying bacterial activities, as reported in the literature [20]. High nitrite level (more than 0.10 mg-N/L) and low total chlorine residual (<0.5 mg/L) implied the samples collected from R-5

Table 1
Details of chemical parameters in the samples collected from R-2 and R-5

Parameters	Origin of samples	
	R-2	R-5
Total chlorine (mg/L)	1.89 ± 0.03	0.11 ± 0.03
TAN** (mg/L)	0.450 ± 0.008	0.072 ± 0.002
Nitrite (mg-N/L)	0.010 ± 0.002	0.285 ± 0.006
Nitrate (mg-N/L)	0.060 ± 0.004	0.195 ± 0.007
NO_x*** (mg-N/L)	0.070 ± 0.006	0.480 ± 0.004
TIN* (mg/L)	0.520 ± 0.014	0.550 ± 0.015
DOC (mg/L)	2.76 ± 0.20	2.72 ± 0.20
pH	7.96 ± 0.10	7.64 ± 0.10

Notes: *TIN (total inorganic nitrogen): summation of TAN and NO_x.
**TAN: summation of NH_3–N, NH_4^+–N and N associated in NH_2Cl.
***NO_x: summation of nitrite and nitrate.

were severely nitrifying [3]. Similarly, low nitrite residual (⩽0.01 mg-N/L) and chloramine residual of 1.89 ± 0.03 mg/L demonstrated the samples collected from R-2 were mildly nitrifying [3].

3.2. *Profiles of total chlorine and nitrogenous compounds in rechloraminated bulk water samples*

In mildly nitrified water, a slow decay of total chlorine with mostly stable nitrogenous compounds (Fig. 2) was noted when they were rechloraminated. This is similar to the results reported elsewhere [12,21]. However, a noticeably fast TAN drop was observed within the first 24 h of incubation. TAN loss within the first 24 h (0.039 ± 0.013 mg/L) was similar to the subsequent 814 h (0.04 ± 0.012 mg/L). The nitrite and nitrate profiles were stable (Fig. 2). TIN decreased by 0.069 ± 0.015 mg/L, which was the same as TAN loss (0.079 ± 0.013 mg/L). In contrast to this behavior, TIN losses were not observed for samples traveling from R-2 to R-5 in the laboratory scale system and hence, the TIN loss seemed to be induced by rechloramination in microbes eliminated samples.

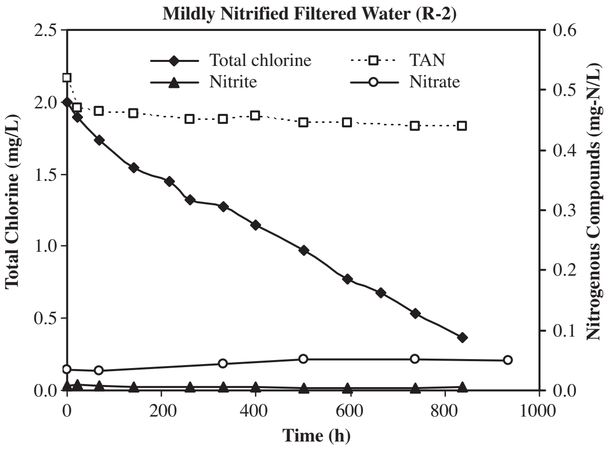

Fig. 2. Total chlorine and nitrogenous compounds profiles in the mildly nitrified (collected from R-2) water after eliminating the microbes through filtration.

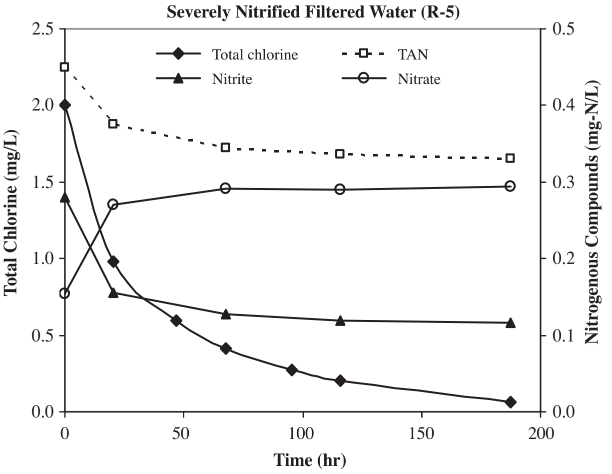

Fig. 3. Total chlorine and nitrogenous compounds profiles in the severely nitrified (collected from R-5) water sample after eliminating the microbes through filtration.

In severely nitrified water, significantly accelerated total chlorine loss was observed (Fig. 3) which is similar to our earlier observation [12,21]. Similarly, rapid TAN and nitrite losses were associated with chloramine decomposition in the first 24 h of incubation. TAN and nitrite were lost by 0.079 ± 0.012 mg/L and 0.13 ± 0.006 mg-N/L, respectively, and the losses continued at a slower rate in the later period. The TIN mass balance was carried out at the beginning and end of the experiment. The TIN loss was 0.140 ± 0.024 mg/L during incubation, which is close to the TAN loss (0.114 ± 0.012 mg/L). Nitrite loss was associated with nitrate gain (Fig. 3). Similarly, nitrate gain (0.145 ± 0.009 mg-N/L) was closer to nitrite loss (0.164 ± 0.006 mg-N/L). Again if the laboratory scale system is considered, there were no TIN losses between R-2 and R-5 (Table 1) and hence, the TIN loss should have been induced by the rechloramination in microbes eliminated samples. Nitrite oxidation rate in the sample is 0.006 mg-N/(L*h) (Table 1).

3.3. *Chemical chloramine decay mechanisms in rechloraminated samples*

In both mildly and severely nitrified samples, TAN and TIN losses were same (Table 2) and

Table 2
Summary of nitrogen mass balance and chloramine decay mechanisms in mildly and severely nitrified bulk waters

Parameters		*Mildly nitrified water (R-2)	**Severely nitrified water (R-5)
***TAN loss (mg-N/L)		0.069 ± 0.013	0.116 ± 0.010
†TIN loss (mg-N/L)		0.079 ± 0.015	0.140 ± 0.024
Nitrite loss (mg-N/L)		0.005 ± 0.002	0.164 ± 0.006
Nitrate gain (mg-N/L)		0.015 ± 0.002	0.144 ± 0.012
Chloramine demand by (mg-Cl_2/L)	Auto-decomposition (Eq. (3))	0.52 ± 0.098	0.87 ± 0.08
	Nitrite oxidation(Eq. (1))	0.03 ± 0.03	0.82 ± 0.03
Total chloramine demand (mg-Cl_2/L)		0.55 ± 0.13	1.69 ± 0.11
Chloramine remaining in sample (mg-Cl_2/L)		0.39 ± 0.03	0.09 ± 0.03
Chloramine demand by other mechanisms (mg-Cl_2/L)		1.06 ± 0.19	0.22 ± 0.17

Notes: *Changes observed within the first 840 h of incubation were considered.

**Changes observed within the first 180 h of incubation were considered.

***TAN: summation of NH_3-N, NH_4^+-N and N associated in NH_2Cl.

†TIN: summation of TAN and NO_x.

occurred in the presence of chloramine and in the absence of microbes. Hence the TAN is assumed to be converted into nitrogen gas, most possibly by auto-decomposition (Eq. (3)). Moreover, analysis of adenosine triphosphate in the filtered samples confirmed the effectiveness of filtration (0.2 µm polycarbonate membrane filter) in removing microbes (data not presented). Similarly, nitrate gain was closer to nitrite loss (Table 2) which indicated an abiotic nitrite oxidation (Eq. (1)).

In the mildly nitrified water, chloramine loss by auto-decomposition within the first 24 h of incubation was 0.29 ± 0.10 mg-Cl_2/L and actual loss was 0.17 ± 0.06 mg-Cl_2/L which are same. When whole incubation period (840 h) was considered the chloramine loss by auto-decomposition was 0.52 ± 0.09 mg-Cl_2/L, whereas the loss due to other mechanisms was 1.06 ± 0.19 mg-Cl_2/L in the mildly nitrified water (Table 2). It could be noted that the loss took place over a prolonged incubation time (840 h) at a very slow rate. According to Vikesland [7], NOM oxidation process is slow, but can significantly impact in chloramine decay. Therefore, NOM oxidation is assumed to play a key role in accelerating chloramine decay in the later part of the curve. Nitrite level was low and hence nitrite oxidation contributed less to the decay.

In the severely nitrified water, the major chloramine decay mechanisms were auto-decomposition (0.87 ± 0.08 mg-Cl_2/L) and nitrite oxidation (0.82 ± 0.03 mg-Cl_2/L). The chloramine loss by other mechanism including NOM oxidation was 0.22 ± 0.17 mg-Cl_2/L, which is within the experimental error. In the mildly nitrified water, about 26% of chloramine was demanded by auto-decomposition whereas in the severely nitrified water, 85% was consumed by both nitrite oxidation and auto-decomposition. Other mechanism(s), possibly NOM oxidation, was dominant in the mildly nitrified water but could not be associated with NOM from measurements. However, all the losses could be explained in the severely nitrified water.

3.4. Effect of nitrite addition on chloramine decay mechanism in mildly nitrified samples

A significant effect of nitrite (0.28 mg-N/L) on chloramine decay was observed (Fig. 4). The decay rate before addition of nitrite was 0.0017 ± 0.0002 h^{-1}, but after the addition of nitrite it was 0.0045 ± 0.0009 h^{-1} which is similar to the decay rate reported elsewhere [12,15]. Nitrite loss rate was 0.0021 mg/

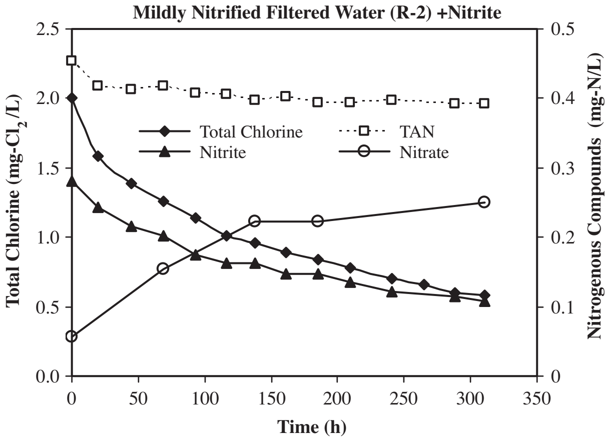

Fig. 4. Total chlorine and nitrogenous compounds profiles in the mildly nitrified (collected from R-2) filtered water after addition of nitrite.

Table 3
Percentage of chemical chloramine demand by different mechanisms

Bulk water samples	Cloramine loss (%) by various mechanisms		
	Auto-decomposition	Nitrite oxidation	Other mechanisms*
Mildly nitrified (R-2)	32	1.9	66
Mildly nitrified (R-2) + nitrite	32	51	18
Severely nitrified (R-5)	46	43	12

Note: *Mostly thought to be due to NOM oxidation if above experimental error.

(L*h) in the first 24 h which is substantially less compared to that in severely nitrified water. Similar to the previous results, the same rapid TAN loss (0.041 ± 0.01 mg/L) was noted in the first 24 h compared to the rest of the period. As in the previous section, chloramine losses were calculated at the end of the experiment (310 h of incubation). Calculated chloramine losses from auto-decomposition and nitrite oxidation were 0.53 ± 0.1 and 0.85 ± 0.03 mg-Cl_2/L, respectively, whereas the loss by unknown mechanisms was 0.30 ± 0.18 mg-Cl_2/L which is significantly less compared to mildly nitrifying sample without the addition of nitrite. This could be due to two reasons. Firstly, the nitrite oxidation could have dominated after the addition of nitrite, possibly due to more favorable direct reaction between chloramine and nitrite than other chemical reactions under normal water conditions as detailed elsewhere [13,16]. Secondly, the reaction took place within the 300 h compared to 840 h in the nonnitrite added sample.

3.5. Summary of chemical decay mechanisms in rechloraminated samples

Chloramine losses by different mechanisms in rechloraminated, mildly, and severely nitrified waters under various conditions are presented in Table 3. Nitrite oxidation and auto-decomposition are normally affected by different parameters (pH, Cl-to-TAN ratio, and temperature). Therefore, they had been adjusted to be the same in all experiments. The loss that could not be explained by Eqs. (1) and (3) was assigned to decay by mechanisms such as NOM oxidation. Unknown mechanisms were foremost (66%) in the mildly nitrified water when the nitrite residual was <0.01 mg-N/L, but it took very longtime to realize the loss and hence it is assumed to be contributed by the slow NOM oxidation. However, after the addition of nitrite (0.28 mg-N/L), about 82% of loss could be explained by auto-decomposition and nitrite oxidation (Table 3). In the severely nitrified water, auto-decomposition (46%) and nitrite oxidation (42%) could be explained by the majority of chloramine loss when the re-chloramination was carried out by dosing 2.0 mg-Cl_2/L of chloramine. These results suggest that the failure by utilities to successfully rechlorinate severely nitrified waters must be due to the role of auto-decomposition and nitrite oxidation possibly induced by SMPs or modified NOM characteristics. The results suggest that major mechanisms of chloramine loss could be evaluated if one considers stoichiometry, although kinetic evaluation is needed to better understand the contribution of each mechanism.

3.6. Implications of the study to full-scale system operation

Three major uses can be derived from the conclusion of this study:

Firstly, chloramine loss by the suspected NOM oxidation would not greatly impact on chloramine stability. In the mildly nitrified water, the major mechanism accelerating chloramine decay is suspected to be NOM oxidation, as other measurements had not been made. However, the NOM oxidation takes place slowly as it took 840 h to decay all chloramine (2.0 mg-Cl_2/L). In the other samples, chloramine dropped faster, allowing only a short time for NOM oxidation. Hence, the unknown mechanism or NOM oxidation did not contribute much. Normally, a maximum retention time in the distribution system is about 7 days or 154 h and hence, NOM oxidation is unlikely to play a major role in determining the stability of chloramines in full-scale systems.

Secondly, during rechloramination, undesirably, some ammonia can be lost. It took place in the initial few hours of rechloramination. In the full-scale system, once this time is passed after initial chloramination, it is unlikely to create substantial chloarmine loss. However, when water utilities boost chlorine in the later stages, it can affect the original aim if chloramine is also lost along with ammonia.

Thirdly, in severely nitrifying waters, attempt of utilities to recover the lost residual by rechloramination can be greatly controlled by both auto-decomposition and nitrite oxidation. Because most of the chloramines loss can be explained by these two mechanisms, and possibly the reason why utilities find it difficult to recover even after rechloramination, the reaction might be catalytic.

Finally, in severely nitrifying waters, SMPs or modified NOM heavily accelerate chloramine decay [12] and hence, understanding what controls the production of the SMP and developing proper control measures are important.

4. Conclusions

Experiments were conducted to understand the chloramine decay mechanisms, using stoichiometry calculations in the mildly and severely nitrified bulk waters when they were subjected to rechloramination. The samples used for these experiments were obtained from laboratory scale systems and the major conclusions made in this study are as follows:

- Rechloramination leads to ammonia losses at the initial few hours.
- According to the stoichiometry calculations, unknown mechanisms (most probably NOM oxidation) were dominant in mildly nitrified water at low nitrite concentration (<0.01 mg-N/L), especially when prolonged decay took place. However, nitrite oxidation and auto-decomposition can explain about 83% of chloramine loss after the addition of nitrite (0.28 mg-N/L).
- Most chloramine loss (85–88%) could be explained by nitrite oxidation and auto-decomposition in the severely nitrified waters.
- Application of stoichiometry was found to be useful in determining possible chloramine decay mechanisms.

Acknowledgments

The authors acknowledge the funding offered by Curtin University, Western Australia, Australian Research Council (ARC Linkage project: LP0776766) and Water Corporation. The authors would like to acknowledge George Kastl who designed the system which is used for this experiment when he was an employee of Sydney Water Corporation. Acknowledgments are also to Sydney Water Corporation for allowing us to use the design.

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